

1. INTRODUCTION

The Desert Research Institute (DRI) and Sonoma Technology, Inc. (STI) are conducting a study of the causes of higher ozone levels on weekends in the South Coast Air Basin (SoCAB). The proposed work is being conducted in three phases over a period of 30 months. In phase I, a retrospective analysis of existing ambient air quality and meteorological data for the South Coast Air Basin is intended to improve current conceptual understanding of the physical and chemical processes that drive the “weekend effect” and to refine our working hypotheses for the study. In phase II, a field measurement program will be conducted during summer-fall 2000 to collect and assemble air quality and emission activity databases to test our hypotheses. The data analyses during phase III include temporal and spatial variations in ozone, ozone precursors, and emission source indicators (e.g., carbon monoxide [CO], nitric oxide [NO], total and speciated non-methane hydrocarbons [NMHC], and elemental carbon [EC]), time-resolved hydrocarbon source apportionment, analysis of emissions activity data, evaluation of the weekend effect by semi-empirical methods and review of air quality model simulations of Southern California Ozone Study (SCOS97-NARTSO) episodes.

This report summarizes the analysis of available air quality and emissions inventory data during Phase I of the study. This study is supported by the National Renewable Energy Laboratory and the Coordinating Research Council, and is conducted in coordination with the California Air Resources Board (ARB). Information on the progress of this and other current studies of the weekend effect in California is available at following ARB web site.

<http://www.arb.ca.gov/aqd/weekendeffect/weekendeffect.htm>

1.1 Findings of Past Studies

Since the mid 1970's it has been documented that ozone levels in the California's South Coast Air Basin are higher on weekends than on weekdays, in spite of the fact that ozone pollutant precursors are lower on weekends than on weekdays (Elkus and Wilson, 1977; Horie et al., 1979; Levitts and Chock, 1975; Zeldin et al., 1989; Blier and Winer, 1998; and Austin and Tran, 1999). Similar effects have been observed in San Francisco (Altshuler et al. 1995) and the northeastern cities of Washington D.C., Philadelphia, and New York (SAIC, 1997). While a substantial WE effect has been observed in these cities, the effect is less pronounced in Sacramento (Austin and Tran, 1999), and is often reversed in Atlanta (Walker, 1993) where VOC/NOx ratios are typically higher. Several of the above studies show that the weekend effect is generally less pronounced in downwind locations where ambient VOC/NOx ratios are higher. Past studies of the weekend effect in the South Coast Air Basin have produced the following conclusions.

WE/WD Differences in Ozone

- The distribution by day-of-the-week of the ten highest ozone concentrations in the Basin for each year for each station in the period 1986-93, showed these episodes occurred significantly more often on Saturdays than on Sundays through Wednesdays. (Blier and Winer, 1996)

- During 1992-94, the typical pattern for ozone in many sites in Los Angeles is a large increase from Friday to Saturday, no change or slight decrease from Saturday to Sunday, then a large decrease from Sunday to Monday. (Austin and Tran, 1999)
- During 1992-94 at Los Angeles-N. Main, adjusted daily maximum ozone increased 31% from Friday to Saturday, increased slightly (1%) on Sunday, then decreased 28% on Monday. Lynwood, Pasadena, and Pico Rivera share a similar pattern to downtown L.A. (Austin and Tran, 1999).
- The weekend effect is least pronounced at transport sites far downwind. The further downwind a site is, the milder the weekend effect (e.g., Lake Gregory, Banning, Hemet, Perris, and Santa Clarita). Coastal sites (Hawthorne and West Los Angeles) also exhibit a mild weekend effect (Austin and Tran, 1999).
- Many sites show a “Sunday effect” in the 1996-98 period (Austin and Tran, 1999).
- Decreases in peak ozone levels during the decade from the mid-1980 to mid-1990 were greatest in the western and middle portions of the SoCAB. On average there were greater reductions on weekdays than on weekends and hence the differences in WD vs. WE ozone maxima increased in the 1990s over the 1980s (Blier and Winer, 1996).

WE/WD Differences in Ozone Precursors Concentrations

- On average, early morning ambient concentrations of NO₂ and NO_x 1986-93 were lower by approximately 20-25% and 30-50%, respectively on weekend days than on typical weekdays in the Coastal/Metropolitan region of the SoCAB. (Blier and Winer, 1996)
- NO_x is uniformly lower on Sunday than other days except at midnight to 4 a.m. when it is comparable with weekday mixing ratios. Morning NO_x is highest on weekdays, followed by Saturday and lowest on Sunday. Saturday afternoon levels are comparable to or slightly lower than weekday levels. Saturday evening levels tend to be lower than on Friday and roughly equal to or higher than the mean weekday evening levels.
- The reactivity of the ambient hydrocarbon mixture has dropped between 1995 and 1996. Reactivity appears slightly lower on weekends (Franzwa and Pasek, 1999).

WE/WD Differences in Ozone Precursor Emissions

- On-road motor vehicles are the single largest source category for ozone precursor pollutants, accounting for about 45%, 64%, and 69% of average daily reactive organic gases (ROG), NO_x, and CO, respectively. Studies since 1987 have shown that mobile source emissions are substantially underestimated compared to emissions models. Most of the on-road emissions are due to gasoline vehicles, but diesel vehicles contribute substantially to NO_x emissions. The vast majority of CO emissions are associated with on-road and other mobile sources.

- Second to on-road mobile sources, stationary and area-wide sources are significant sources of ROG, while other mobile sources are currently a less important source of ROG. In contrast, other mobile sources generate relatively large emissions of NO_x, while stationary and area-wide sources are less important NO_x contributors.
- Mobile sources, estimated to be the most important contributor of ozone precursor emissions in the SoCAB, are known to follow pronounced weekday-weekend patterns of activity. There are many measures of on-road travel activity and several ways to compare them between weekdays and weekends. A few examples are: vehicle miles traveled (VMT), vehicle speeds, fleet mix (trucks vs cars), cold/warm engine starts, trip frequency and length, trip geographic patterns, trip chaining, cars (SUVs vs commute cars), and diurnal patterns.
- Urban freeway traffic builds gradually from Monday through Friday, drops off on Saturday, and drops even further on Sunday. Rural and recreational routes experience minimum traffic volumes at mid-week, with pronounced peaks on Friday and Sunday. This result has been repeated for numerous urban centers, especially for Los Angeles.
- In a 1993-95 study of Los Angeles vehicles equipped with data loggers Magbuhat and Long (1996) showed that the frequency of cold starts follows the same general pattern as urban traffic volumes.
- Several U.S. EPA reports document weekend-weekday activity information. Two recent EPA publications (Glover and Brzezinski, 1998a and 1998b), reflect the results of instrumented vehicle studies in Spokane and Baltimore. Glover and Brzezinski concluded that weekend urban travel is less than weekday travel and that most weekend travel tends to begin at a later hour of day than weekday travel with relatively uniform traffic throughout the day.
- Several years ago, staff from the SCAQMD in Los Angeles used Caltrans traffic count data to contrast average weekday vs. average weekend traffic counts, for all vehicle types. They found that weekend travel counts were approximately 96 percent of weekday travel counts, and that weekend travel occurred more uniformly throughout the day, as opposed to having pronounced peak periods characteristic of weekday travel.
- More recently, SCAQMD staff attempted to use truck traffic counts to better understand weekend vs. weekday heavy duty vehicle activity. They have roughly estimated weekend truck traffic counts to be approximately 40 percent of the truck traffic observed during an average weekday (Hsiao, 1999). The opposite phenomenon is observed for recreational boating patterns in California. Weekend recreational boating activity is 6 to 8 times larger than weekday activity.

The weekend effect has generated strong interest because of its potential implications for ozone control strategies. Much of the difficulty in addressing the ozone problem is related to ozone's complex photochemistry in which the rate of O₃ production is a non-linear function of the mixture of volatile organic compounds (VOC) and oxides of nitrogen (NO_x) in the atmosphere. Depending upon the relative concentration of VOC and NO_x and the specific mix of

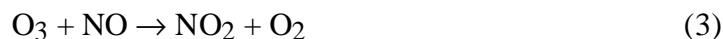
VOC present, the rate of O₃ formation can be most sensitive to changes in VOC alone or to changes in NO_x alone or to simultaneous changes in both VOC and NO_x. Understanding the response of ozone levels to specific changes in VOC or NO_x emissions is fundamental to understanding why ozone is higher during weekends in the South Coast Air Basin.

1.2 Fundamentals of Ozone Photochemistry

The only significant chemical reaction producing ozone in the atmosphere is the reaction of atomic and molecular oxygen. At lower altitudes, where only UV-radiation with wavelengths greater than 280 nm is present, the only significant oxygen atom production is from photodissociation of nitrogen dioxide (NO₂) into nitric oxide (NO) and ground state oxygen atoms, O(³P), Reaction (1). The ground state oxygen atoms react with molecular oxygen to produce O₃, Reaction (2), (where M is a third body such as N₂ or O₂).



When nitrogen oxides are present, O₃ reacts rapidly with NO to regenerate NO₂, Reaction (3).



The first and third reactions occur rapidly, establishing a steady-state equilibrium ozone concentration [O₃] that is determined by the "NO-photostationary state equation", Equation (4)

$$[\text{O}_3] = \frac{J_1[\text{NO}_2]}{k_3[\text{NO}]} \quad (4)$$

where J₁ is the photolysis frequency of Reaction (1), k₃ is the rate constant for Reaction (3), [NO₂] is the concentration of nitrogen dioxide and [NO] is the concentration of nitric oxide. Because these reactions only recycle O₃ and NO_x, they are insufficient, by themselves, to create excessive ozone levels.

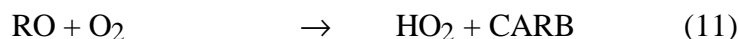
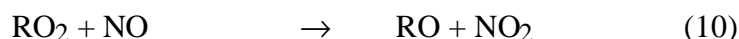
When carbon monoxide or volatile organic compounds are present, however, their oxidation produces hydroperoxy radical (HO₂) and organic peroxy radicals (RO₂) which react with NO to form NO₂ without destruction of ozone, thereby allowing ozone to accumulate. A fraction of O₃ photolyzes to produce an excited oxygen atom, O(¹D).



A fraction of these react with water to produce hydroxyl (HO) radicals.



Other sources of HO radicals include the photolysis of carbonyl compounds and smaller contributions due to nitrous acid (HONO) and other radical precursors. The HO radicals react with CO or organic compounds (RH) to produce peroxy radicals (HO₂ or RO₂). The peroxy radicals react with NO to produce NO₂ which photolyzes to produce additional O₃:



The net reaction is the sum of Reactions (8) through (12) plus twice Reactions (1) and (2):



where CARB is either a carbonyl species, either an aldehyde (R'CHO) or a ketone (R'CR''O). The carbonyl compounds may further react with HO or they may photolyze to produce additional peroxy radicals that react with NO to produce NO₂ (Seinfeld, 1986; Finlayson-Pitts and Pitts, 1986). Peroxy radical reactions with NO reduce the concentration of NO and increase the concentration of NO₂. This reduces the rate of Reaction (3), which destroys O₃ and increases the rate of reaction (1) that produces ozone. The increase in the ratio of [NO₂]/[NO] leads to higher O₃ concentration according to Equation (4).

For the majority of VOCs emitted from anthropogenic and natural sources, reaction with the hydroxyl radical is the major cause of chemical change. Acetylene, most of the smaller alkanes, and benzene have lifetimes which exceed the typical summer residence time of air masses in the South Coast Air Basin (~12 hours, Douglas et al., 1991). Most of the other hydrocarbons will retain their relative abundances to other species when emissions are fresh but will have substantially changed in proportion to the other species after the air mass containing them has aged for a few hours. The degradation reactions for all classes of VOCs, in addition to the conversion of NO to NO₂ and the formation of ozone, lead to the formation of carbonyl compounds (aldehydes, ketones, hydroxycarbonyls, and dicarbonyls), organic acids, organic nitrates (including peroxyacyl nitrates, the simplest member of which is peroxyacetyl nitrate [PAN]). PAN thermally decomposes back to its reactants, NO₂ and acetylperoxy radical. Thus, PAN can serve as a nighttime reservoir for NO_x and means of transport of NO_x to downwind areas. Carbonyl compounds that are produced from hydrocarbon oxidation can be important

reactive VOCs themselves, and thus important sources of peroxy radicals responsible for ozone production.

In the lower troposphere the formation of HNO_3 by reaction of NO_2 with HO is a major sink of NO_x because HNO_3 reacts slowly in the lower troposphere and it is rapidly removed due to dry and wet deposition. Reaction of HNO_3 with ammonia (NH_3) yields particulate ammonium nitrate (NH_4NO_3), which is in equilibrium with NH_3 and HNO_3 at typical summertime temperatures in southern California. NO_x can also be removed during the night through heterogeneous reactions of nitrogen pentoxide (N_2O_5) on water coated aerosol particles. N_2O_5 is produced by the reaction of NO_2 with nitrate radicals (NO_3), which are produced by the reaction of NO_2 with O_3 . Because NO_3 radicals rapidly photolyze and react rapidly with NO , concentrations of the NO_3 radical and N_2O_5 remain low during daytime but can increase during evening and nighttime hours in the absence of NO .

1.3 Importance of VOC/ NO_x Ratio in Ozone Formation

The hydroxyl radical is the key reactive species in the formation of ozone. The reaction of HO with VOC initiates the oxidation sequence. However, there is a competition between VOCs and NO_x for the HO radicals. Figure 1.3-1 shows the linkages among the reactions that propagate radicals and those that remove them. VOCs are consumed in the sequence of ozone formation, while both HO/HO_2 and NO_x act as catalysts. Termination occurs when HO_2 combine to form hydrogen peroxide (H_2O_2) or by reaction of HO with NO_2 to form HNO_3 . The production efficiency of O_3 per molecule of NO_x varies with total concentration of NO_x and the ratio of VOC to NO_x . At low VOC-to- NO_2 ratios, HO reacts predominantly with NO_2 , removing radicals and retarding O_3 formation. Under these conditions, a decrease in NO_x concentration favors O_3 formation. High ratios of VOC to NO_x concentration favor HO reaction with VOCs that generate new radicals that accelerate O_3 production. At a sufficiently low concentration of NO_x , or a sufficiently high VOC-to- NO_2 ratio, a further decrease in NO_x favors peroxy-peroxy reactions, which retard O_3 formation by removing free radicals from the system. At a given level of VOC, there exists a NO_x mixing ratio at which a maximum amount of ozone is produced. This optimum VOC/ NO_x ratio depends upon the reactivity to HO of the particular mix of VOCs present. For ratios less than this optimum ratio, increasing NO_x decreases ozone.

Ozone isopleth diagrams are used to represent the dependence of O_3 production on the initial amounts of VOC and NO_x . Figure 1.3-2 is an example of an ozone isopleth plot generated using the Ozone Isopleth Plotting Program, Research Version (OZIPR) with the RADM2 chemical mechanism (Stockwell et al. 1990). To generate this plot, ozone formation is simulated in a hypothetical well-mixed box of air from ground to the mixing height that is transported from an urban center to a downwind location of maximum ozone concentrations. Multiple simulations are performed with varying initial concentrations of NO_x and anthropogenic VOC.

The ozone ridge in Figure 1.3-2 corresponds to the maximum O_3 concentration that can be achieved at a given VOC level. The VOC/ NO_x ratio at the ridgeline is about 10 to 12. The HO radical chain length, which is the number of times a newly formed HO radical is regenerated through radical chain propagation before it is destroyed, reaches a maximum at this VOC/ NO_x ratio. Thus, the ridgeline corresponds to the VOC/ NO_x ratio at which O_3 is most efficiently formed. Above the ridgeline a reduction in NO_x lowers the rate at which OH and NO_2 are

removed by formation of HNO_3 and leads to an increase in maximum O_3 . This region is commonly described as “radical-limited” or “hydrocarbon-limited” (i.e., lowering VOC most effectively reduces O_3). “ NO_x -disbenefit” refers to a situation when NO_x reduction leads to an increase in ozone. Below the ridgeline at low NO_x concentrations there is a large region where large reductions in VOC have practically no effect on maximum O_3 . This region is described as “ NO_x -limited.”

The instantaneous VOC/ NO_x ratios tend to increase during transport because HO reacts more rapidly with NO_2 than with VOCs. Thus NO_x is removed more rapidly from the system than VOCs and accounts for the tendency for ozone formation to be NO_x -limited in far downwind areas. Consequently, variations in VOC/ NO_x ratios can exist within air basins, resulting in either NO_x -limited or hydrocarbon-limited areas depending upon the time of day and pattern of pollutant transport. Changes in the spatial and temporal variations of VOC/ NO_x ratios due to day-of-the-week changes in VOC and NO_x emissions must be a key factor in the magnitude and spatial extent of the weekend effect.

1.4 Spatial Variation in Ozone Trends

Ozone trends in the South Coast Air Basin reveal a dramatic step change since the beginning of the decade of the 1990s. Figure 1.3-3 shows the number of annual exceedances of the federal 1-hour National Ambient Air Quality Standard (NAAQS) for ozone in the South Coast Air Basin from 1976 to 1999. The number of ozone standard exceedances within the basin held relatively constant during the 1970s and 1980s, but declined sharply (about two-thirds) in the 1990s. Along with this step change in the ozone trend, Figure 1.3-3 shows that the location of highest maximum 1-hour ozone concentrations has shifted from the central portion of the basin (e.g., Glendora) to the eastern end of the basin (e.g., Lake Gregory). These temporal and spatial changes in O_3 , VOC, and NO_x that have occurred in the basin over the past three decades is a testament to the nonlinear nature of the ozone formation process.

Ambient ozone trends are governed by changes in the temporal and spatial patterns of precursor emissions. Much of these changes are driven by emission control measures in the state implementation plans. The nation’s ozone strategy in the decades of the 70s and 80s favored VOC control over NO_x control based on the premise that VOC/ NO_x ratios in most ozone nonattainment areas were in the below-10 range. Despite two decades of increasingly more stringent emission controls, progress toward attainment of the ozone standard during this period was extremely slow, and the National Research Council (NRC) Committee on Tropospheric Ozone Formation and Measurement concluded that the 20-year effort to attain the ozone NAAQS had largely failed (NRC, 1991). The NRC Committee suggested that past ozone control strategies might have been misdirected due to a significant underestimation of anthropogenic VOC emissions.

Studies have shown that the weekend effect has become more pronounced during the 1990s. At the same time ozone has dropped sharply and the maximum ozone concentrations have shifted eastward. These observations suggest that ozone formation was NO_x -limited prior to the 1990 and that two decades of VOC reductions were largely ineffective until VOC/ NO_x ratios finally began to approach the ridgeline at the end of the 1980s. Since that time, a transition to VOC-limited ozone formation in all but the eastern edge of the basin is most likely responsible

for the sharp reduction in ozone during the 1990s. Studies have also shown that anthropogenic NO_x emissions in the SoCAB are generally lower on weekends, especially during the ozone inhibition period. Areas that do not exhibit a weekend effect are NO_x-limited while areas that do are hydrocarbon-limited. The weekend effect may serve as an indicator that ozone formation in the area is VOC-limited.

1.5 Project Objectives and Scope

The objective of this project is to use method(s) that can test hypotheses for the causes of higher ozone on weekend in the South Coast Air Basin. A preliminary conceptual explanation of the “weekend effect” is derived from an integration of past retrospective analyses of air quality data. This preliminary conceptual explanation is the basis for the hypotheses, and for the experimental and data analysis approaches that are proposed to test the hypotheses during the summer-fall 2000 field study.

PHASE I: Retrospective Analysis of Ambient and Emissions Data and Refinement of Hypotheses.

STI Task 1: Review available emissions data. Based on available emission inventory data, identify ROG and NO_x sources with the potential to be different on weekends than on weekdays. Summarize the diurnal variations in daily ROG and NO_x emissions by day-of-the-week for these sources. Review the method(s) used to determine temporal variations and evaluate uncertainties and identify alternative methods or additional data that are available to update and improve existing temporal allocation of ROG and NO_x emissions. Work with ARB and the SCAQMD to minimize duplication of effort and ensure that the most effective data acquisition and analysis approaches are taken.

DRI Task 1: Analyze retrospective ozone and ozone precursors. Assemble an air quality database for ozone, carbon monoxide, total non-methane hydrocarbons and nitrogen oxides for routine monitoring sites in the SoCAB with continuous data from 1981 to 1998. From current conceptual explanations of the weekend effect, identify key air quality parameters and their spatial, temporal and statistical distributions that can be used to gain further insight into the weekend effect.

DRI Task 2: Review source apportionment analyses. Review the source apportionment analysis conducted by the Desert Research Institute for SoCAB and characterize the day-of-the-week variations in source contributions. Review available source composition profiles and identify sources for which updated profiles are needed.

STI Task 2: Analyze SCOS97-NARSTO meteorological and 3-D ozone data. Evaluate meteorological conditions during SCOS97-NARSTO intensive operational periods (IOPs) to determine applicability of each weekend and weekday IOP for assessments of the WE effect. For applicable IOPs, characterize the surface and aloft spatial and temporal patterns of ozone and ozone precursors utilizing the aloft ozone data measured by LIDAR and instruments on aircraft. Compare the results to 1987 IOPs and determine if the patterns are similar or different. Compare the 1997 weekend and weekday intensive operational periods. Investigate the influence of the mixing heights and wind patterns on ozone concentrations during applicable weekend and

weekday IOP days. Determine if any of the SCOS97 weekend and weekday IOPs are meteorologically similar in terms of mixing heights, winds, 850 mb temperature, ARB flow type, and synoptic pattern. Develop a matrix of meteorological similarities and differences for the IOP days. Compare the surface and aloft spatial and temporal patterns of ozone and ozone precursors on the IOPs and conceptually quantify the variation in ozone pattern between the weekend and weekday IOP days based on the meteorology. For applicable IOPs, analyze the data from the SCOS97 upper-air meteorological network and evaluate the regional representativeness of the temporal and spatial variations in wind and mixing heights that can be obtained from the two PAMS profilers (at LAX and Ontario) alone. If LAX and ONT are representative, then LAX and Ontario data can be used for historical and future analysis. If not, then more upper-air monitoring networks may be required in the future to spatially represent the winds and mixing heights.

DRI and STI Task 3: Synthesize phase I data analysis and prepare Phase 1 Report. Summarize the results of Phase I data analysis. Compare results from each task. Update hypotheses. Revise conceptual model. Finalize field measurement program.

1.6 Guide to Report

This section has stated the purpose and technical objectives of the study. Section 2 examines key air quality parameters that provide further insights into the underlying causes for the weekend effect in the South Coast Air Basin. Section 3 describes the day-of-the-week variations in source contributions based on prior receptor modeling analysis performed by Desert Research Institute for the South Coast Air Basin. Section 4 describes our plan for field measurements during summer-fall 2000. Sonoma Technology Inc. in Roberts et al. (2000) summarizes available emission inventory data and analysis of the SCOS97-NARSTO upper-air meteorological and three-dimensional ozone data.

Ozone Formation Chemistry

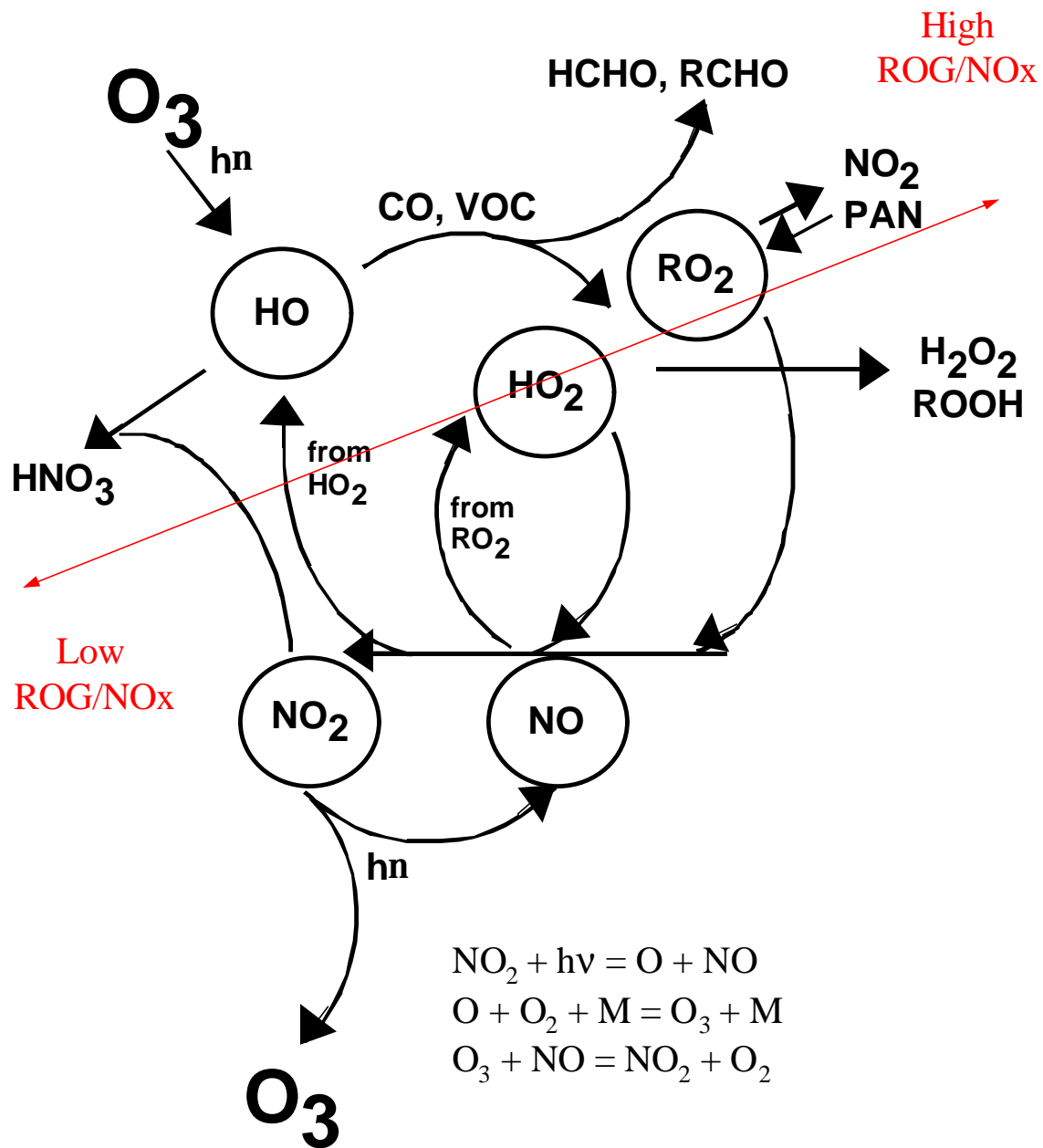


Figure 1.3-1. Schematic of the photochemical pathways leading to the production of ozone in the troposphere and the main termination reactions at high and low VOC/NO_x ratios.

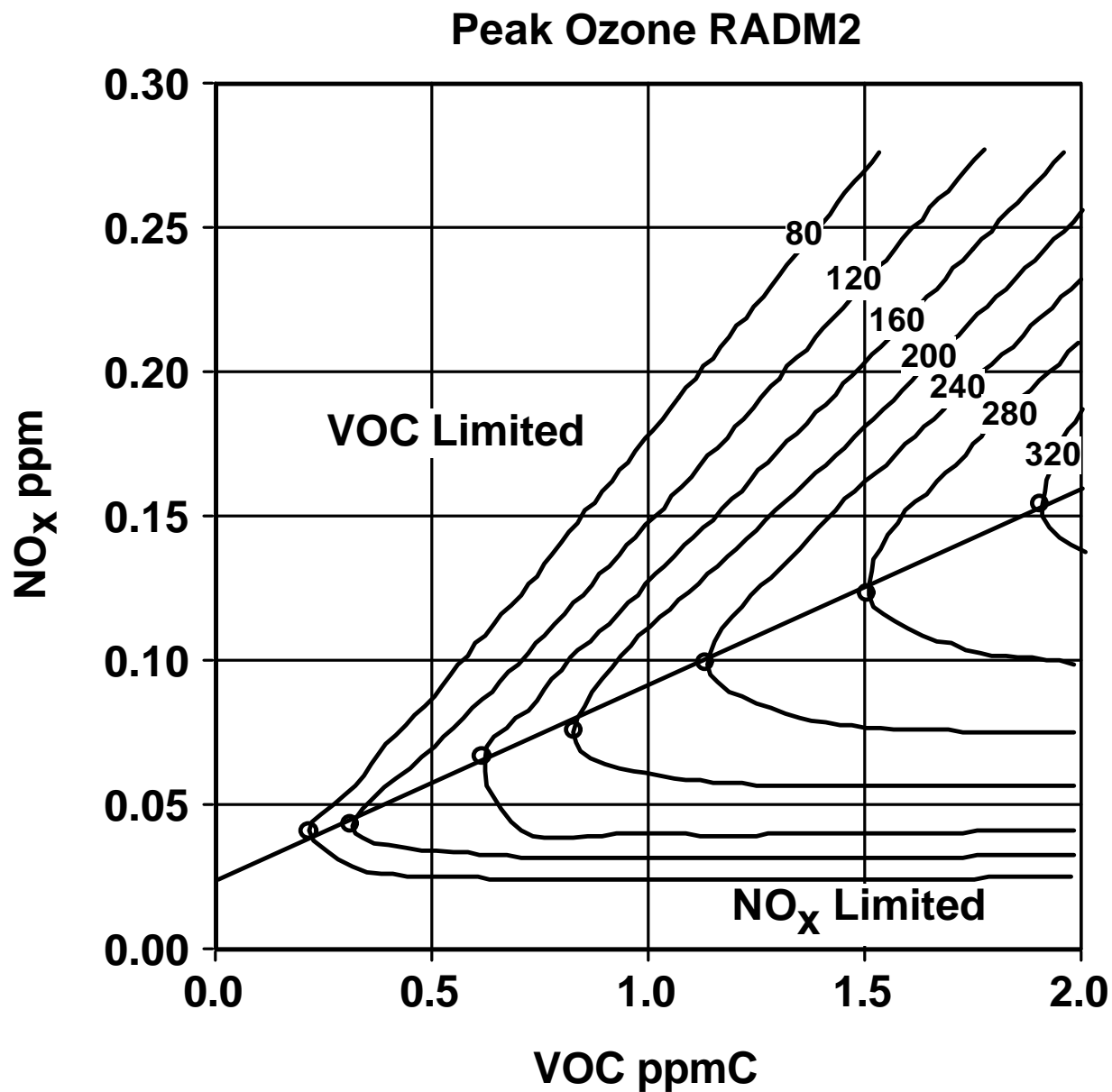


Figure 1.3-2. Typical ozone isopleth plot showing 1-hour maximum ozone concentrations (in ppb) calculated as a function of initial VOC and NO_x concentrations and the regions of the diagram that are characterized as VOC- or NO_x-limited.

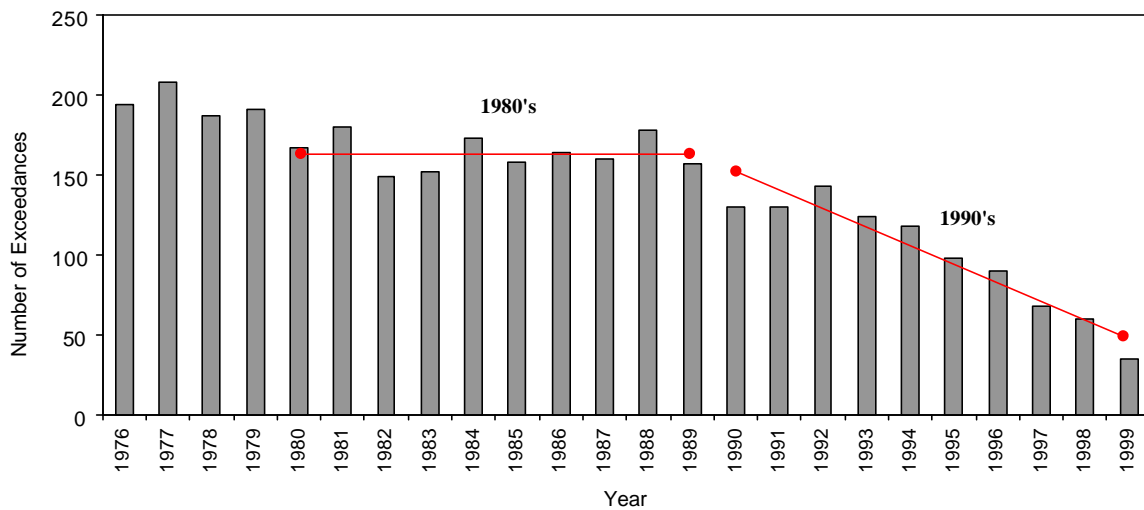


Figure 1.3-3. Trend in number of annual exceedances of the federal 1-hour ozone standard in the South Coast Air Basin from 1976 to 1999.

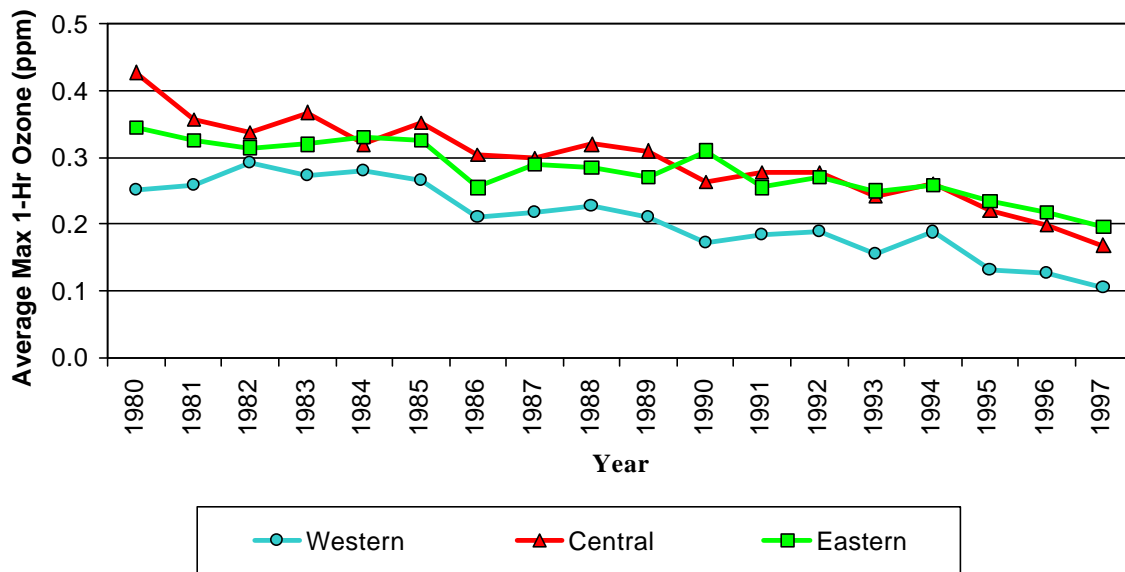


Figure 1.3-4. Trends in average maximum 1-hour ozone from 1980 to 1997 in the western, central and eastern portions of the South Coast Air Basin. Monitoring site included in the averages are Los Angeles – N. Main, Lynwood, N. Long Beach, Anaheim, and La Habra, for Western, Azusa, Glendora, Pomona, and Upland for Central, and Riverside and Lake Gregory for Eastern.